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THE ION-EXCHANGE REMOVAL OF CYANIDE FROM GOLD-MILL WASTES FOR ENVIRONMENTAL BENEFIT

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AUGUST 20, 1976

DECLASSIFIED
DATE 4/1/84
AUTHORIZED BY

30 pp

MINERALS RESEARCH PROGRAM

MINERAL SCIENCES LABORATORIES
REPORT MRP/MSL (CF) 76-26 (IR)

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INTRODUCTION

The purpose of this investigation was to make an ion-exchange pilot-plant study of the practicability of removing cyanide and metal-cyanide complexes from a cyanidation waste effluent. The waste was a filter-press bleed effluent from the Dome gold-cyanidation operation in the Timmins area of Ontario.

The Federal Government of Canada is empowered, by both the B.N.A. Act of 1867 and the amended Fisheries Act of 1970, to control the discharge of deleterious or toxic matter into lakes and streams sustaining fish life. Environment Canada, as an agency of the Canadian Government, has proposed an objective of 0.1 ppm total cyanide (CN_T) for cyanidation effluents discharged to the water environment, (a) to establish environmental guidelines for the gold mining and milling industry, and (b) for the preservation of fish and other aquatic life in our Canadian natural waters. They have already drafted regulations for control of heavy metal content in processed effluents from the base metal, iron ore and uranium mining and milling operations. The specifications are, in ppm, 0.3 Cu, 0.5 Ni and 0.5 Zn[1]. Processed effluents, devoid of toxic concentrations of both cyanide and heavy metals, could be discharged to Canadian watercourses or recycled to mine or mill operations.

Eric Goldblatt[2] recovered cyanide from solution by ion-exchange in a 25 ton/day pilot plant. Toxic cyanides and heavy-metal cyanide complexes were removed from a South African gold-cyanidation waste. The Goldblatt process removed total cyanides by series adsorption on SO_4-form and CuCN-form anion-exchange resins in static columns.

A CANMET feasibility study[3] on the removal of the total cyanide from six different cyanidation wastes confirmed that the ion-exchange process had the potential of, (1) reducing cyanide and heavy metals to meet Canadian environmental objectives, (2) conserving the cyanide and metals for possible reuse, as well as (3) removing thiocyanate (SCN) to <1 ppm should the need arise at some future time. The study further indicated that series adsorption on two SO_4-form anion exchange columns would reduce the total cyanide to environmental objectives of <0.1 ppm. Accordingly, a pilot-plant was set up to further examine the feasibility and economic viability of achieving environmental objectives with the SO_4-form resin system. The gold waste examined was one that had already been looked at in the feasibility study and was considered to be the most difficult[3] yet amenable to eventual full-scale plant treatment as very dilute solutions respond well to ion-exchange technology.

PILOT-PLANT PROCEDURE

The arrangement of equipment for the adsorption, desorption and recovery of the cyanide and heavy metals from the Dome cyanidation waste is shown in Figure 1. This equipment was operated 7½ hours daily.

(a) Adsorption Phase

The cyanidation waste was pumped, "as received" from 50-litre carboys or 45-gallon plastic-lined drums, downflow through two series-connected columns of SO_4-form Amberlite IRA-400*. The SO_4-form of the strong base exchanger was prepared by washing the Cl-form of the "as received" exchanger with 0.1M Na_2SO_4 until no further chloride was indicated by the standard $AgNO_3$ test method.

The 20-inch bed depth of 150 ml of exchanger resin was contained in a 4-ft length of 3/4-inch diameter Kimax brand glass pipe. The progress of total cyanide adsorption, on each column, was followed by a colorimetric analysis[4] of effluent samples. The progress of the thiocyanate adsorption on the lead column of adsorption was followed by another colorimetric analysis[5]. Previous work[3] had indicated that the increase and decrease in effluent thiocyanate concentration was an aid in forecasting the CN_T-loading of the lead column. Ideally, the adsorption flow was to cease when the CN_T-concentration of the end column effluent had attained a breakthrough concentration of 0.1 ppm CN_T, and the lead column had attained an operational CN_T-loading. The lead column was cut out of

*Manufactured and supplied by Rohm & Haas Ltd., Philadelphia, Pa.

* Blue White Industries
Chem-Feed Pump

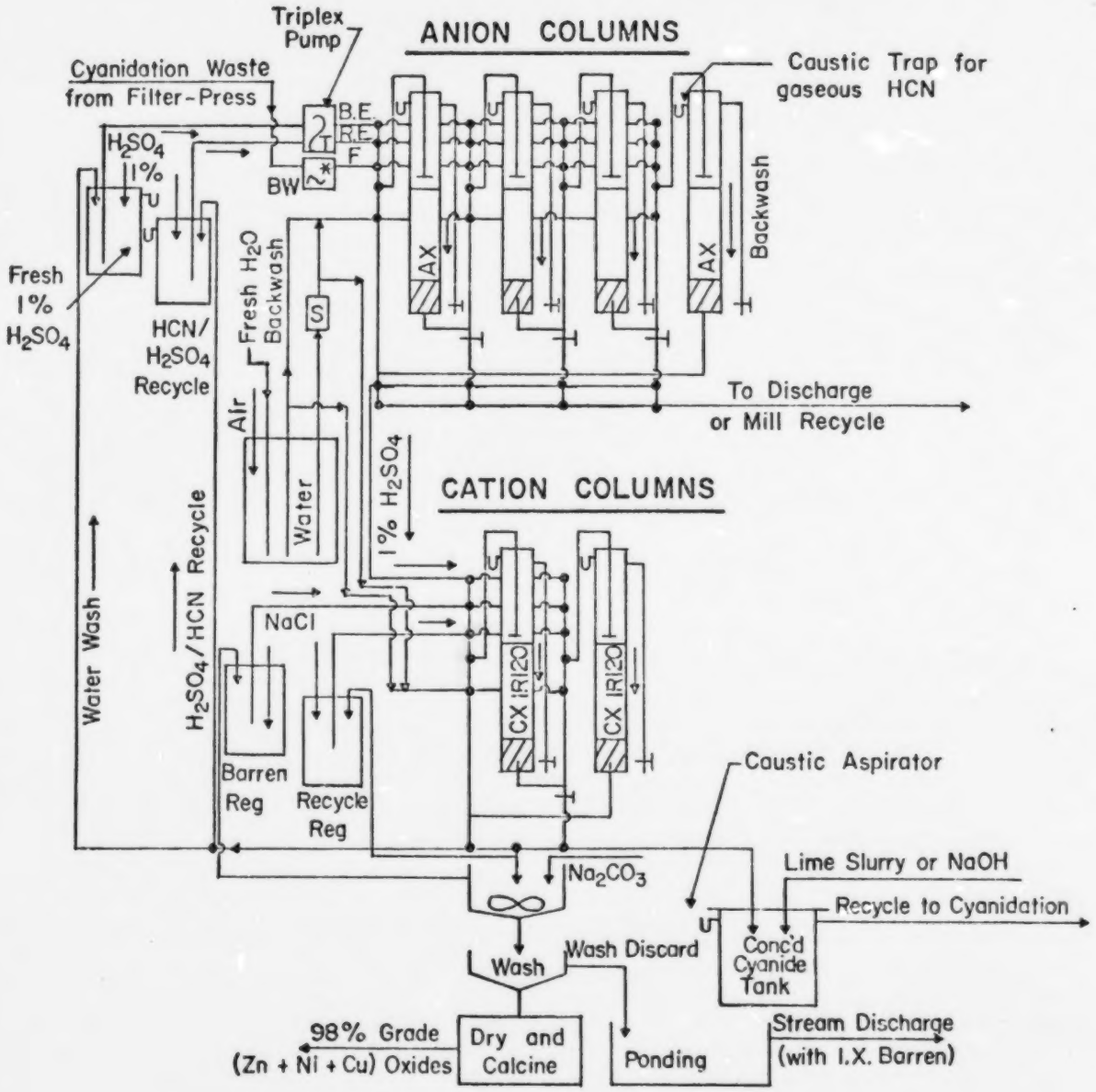

FIGURE 1

PILOT-PLANT ARRANGEMENT
OF STATIC-BEDION-EXCHANGE COLUMNS
FOR TREATING CYANIDATION WASTES

series adsorption after breakthrough from the end column, and the adsorption continued with the former end column in the lead position and a fresh SO_4-form column of resin in the end position. The former lead column was backwashed to displace feed waste and any solids, usually $CaCO_3$, filtered out on the resin bed. This backwash would be returned to cyanidation. The cyanide-loaded column, after backwashing, was ready for the desorption with 1% H_2SO_4.

A concept of the adsorption chemistry is:

Cyanide and Metal-Complex Adsorption

$$2R_ASO_4= + CN^- + M(CN)^{2-}_{3-4} \longrightarrow R_A(CN)^- + R_AM(CN)^{2-}_{3-4} + 2SO_4= \quad (1$$

where R_A= anion exchanger, CN^- = free cyanide and $M(CN)^{2-}_{3-4}$ represents the metal-cyanide complexes in the gold waste, such as Zn $(CN)^{2-}_4$, Ni $(CN)^{2-}_4$ and Cu $(CN)^{2-}_3$.

(b) Desorption Phase

The cyanide-loaded column, after backwashing, was series-connected to a 150-ml resin column of the Na-form exchanger, Amberlite IR-120*. The loaded resin was desorbed by 1% H_2SO_4 downflow through the anion-cation columns.

The acid displaced the free cyanide and decomposed the metal-cyanide complexes on the anion exchanger, as follows:

Cyanide and Metal-Complex Desorption

$$R_A(CN)^- + R_AM(CN)^{2-}_{3-4} + 2H_2SO_4 \longrightarrow R_A2HSO_4 + MSO_4 + 4\text{-}5HCN\uparrow \quad (2$$

*Manufactured and supplied by Rohm & Haas Ltd., Philadelphia, Pa.

where MSO_4 = metal sulphate decomposition product of $M(CN)_{3-4}^{2-}$, and M = Zn, Ni or Cu.

The metal cations, as sulphates, and the hydrocyanic acid gas (HCN) in the anion-exchanger eluate were carried through the cation-exchanger bed. The metal cations were adsorbed as:

Metal Cation Adsorption

$$R_c 2Na + MSO_4 \longrightarrow R_c M + Na_2SO_4 \qquad (3)$$

where R_c = cation exchanger, and M = Zn, Ni, or Cu.

The hydrocyanic acid gas (HCN), carried through the exchange columns in the acid desorption, was collected as a strong fraction in a 1.4N NaOH solution, as:

$$HCN + NaOH \longrightarrow NaCN + H_2O \qquad (4)$$

This free cyanide solution would be recycled to cyanidation. A low fraction of the desorption eluate, where the HCN gas was not detectable with a Dräger tube detector, was recycled for a subsequent cyanide desorption.

Initially, the strong fraction was analyzed for available free cyanide (CNF) by a $AgNO_3$ titration method[6]. Later, both the strong and low fractions were analyzed by the CN_T colorimetric method[4]. Any gaseous HCN not adsorbed in the caustic collector was caught in an aspirator trap (Figure 1) as a safety precaution.

The acid desorption phase was followed by a series upflow water-wash of the anion-cation exchange columns. The purpose of this wash was to, (1) remove acid and soluble cyanide traces in the column, and (2), to convert the bisulphate (HSO_4^-) form of the exchanger back to the SO_4- form for the next cyanide adsorption phase, as:

Water-Wash Conversion

$$2R_AHSO_4^- \xrightarrow[\text{Wash}]{H_2O} R_{A2}SO_4^{=} + H_2SO_4 \qquad (5)$$

Excessive acidic anions on the resin would cause the development of voids of HCN gas in the resin bed during the next adsorption of cyanide and metal-cyanide complexes.

The metal cations were displaced from the cation exchanger by a brine desorption. The resin was simultaneously converted to the Na-form for the next metal adsorption during the acid desorption of cyanide from the anion exchanger bed.

Metal Cation Desorption

$$R_CM + 2\ NaCl \longrightarrow R_C2Na + M(Cl)_2 \qquad (6)$$

The brine desorption of the metals was underway during the adsorption of cyanide on the SO_4- form resin columns.

A strong fraction of the brine desorption was neutralized to ph 8.0 with Na_2CO_3. The low fraction was suitable for recycle to the next metal desorption. The neutralization product was water-washed free of chlorides, dried, calcined and analyzed for metals.

RESULTS

The analyses of the Dome cyanidation waste, used for the cyanide removal study by fixed-bed ion-exchange, is shown in Table 1.

TABLE 1

The Analyses of Dome Cyanidation Waste

Type of Analysis	Dome Cyanidation Waste
Total Cyanide (CN_T) ppm.	14.4 - 67.0
Free Cyanide (CN_F) "	3.0 - 66.5
CNS "	39.8 - 57.8
Total S "	100.0 -170.0
Cu "	8.0 - 15.0
Ni "	2.0 - 4.0
Zn "	0.03- 10.0
NH_3 "	33.0 - 67.0
Au oz./T	< 0.003- 0.003
pH	10.4 - 12.4

The concentration range of the CN_T and of NH_3 shown in this Table is of interest. The cyanide concentration of the feed solution (ie. the cyanidation waste) decreased by a factor of 4.7 times from 67 to 14.4 ppm CN_T during one adsorption cycle. This instability, or "ageing" effect, was noted previously[7]. The 78.5% decrease was disconcerting as it intended to drag out the adsorption phase. Solutions used as feed for ion-exchange treatment are usually reasonably stable and do not change during adsorption. The feed waste would be treated directly from the filter press in an operational mill and the cyanide loss would probably be minimal.

The presence of 33 to 67 ppm NH_3 in the cyanidation waste water may concern the environmentalists. A possible source of ammonia is from underground blasting with ammonia compounds. Ammonia would not be removed in the anion-exchange process. Eliminating or minimizing the entry of ammonia into the mill circuit, and ultimately to the water environment, may be the answer.

(a) Adsorption Phase

The adsorption phases of four cycles are tabulated in Table 2. The CN_T breakthrough volume from the end column in each adsorption phase was exceeded by 154 to 573 bed volumes due to late reporting of analysis from process control. Unless the flow from the end column of a series adsorption ceases when breakthrough occurs (≈0.11 ppm CN_T), the barren effluent becomes contaminated with cyanide concentrations >0.1 ppm CN_T and the barren effluent is no longer discardable.

The difficulty experienced in process control, along with the almost 80% decrease in CN_T concentration of influent waste during adsorption, made it difficult to estimate the degree of loading and the cyanide loading rate.

The cycle 1 adsorption flow rate of 0.73 bed volumes/min on two columns of fresh resin was very fast. Cyanide breakthrough occurred at 1345 bed volumes, but was overshot by 573 bed volumes before control analyses were reported. On cycle 2, at the same adsorption flowrate, breakthrough occurred very early, at 170 bed volumes, but was exceeded by 206 bed volumes before control analyses were received. The early breakthrough was probably due to the overloading on cycle 1. On cycle 3, the adsorption flow was reduced to 0.06 bed volumes/min to allow analytical control to keep pace and to increase volume throughput. Cyanide breakthrough occurred at 600 bed volumes but was overshot by 360 bed volumes before control reported breakthrough. On cycle 4, the adsorption flow was increased to 0.22 bed volumes/min. Breakthrough occurred at 2039 bed volumes and was again exceeded by 154 bed volumes before reported by control.

TABLE 2

ADSORPTION RESULTS

Cycle No.	Cols. on Adsorption	Total Adsorption Time (hrs.)	Retention Time (Min.)		Last Fraction (CN_T ppm)		Barren Effluent			Lead Col. Backwash	
							Volume				
			Nominal Min.	Actual Min.	Lead Col.	End Col.	Litre	Bed Volumes	CN_T ppm	Time hrs.	Bed Volumes
1	A & B	31.03	0.55	0.56	<0.1	<0.1	202	1345	< 0.1	2.78	13.4
2	B & C	3.82	0.55	0.55	0.69	0.11	25	170	< 0.1	2.08	8.3
3	C & D	163.48	-	6.5	0.32	0.11	90	600	< 0.1	1.0	8.8
4	D & A	168.63	1.84	1.85	10.3	<0.10	305.9	2039	< 0.1	0.30	3.5

The end column of this fourth adsorption had already undergone one adsorption/desorption cycle. Figure 2 shows a "royal barren"* curve of the effluent CN_T concentrations during the initial stages of the adsorption on used resin. This displacement volume containing cyanide, representing 92 bed volumes or about 6% of the barren effluent and containing about 0.6 ppm CN_T, could be recycled to cyanidation. Figure 3 shows a curve illustrating the adsorption of cyanide on two SO_4- form columns of Amberlite IRA-400, from a Dome influent waste of variable cyanide concentration.

The investigation was terminated after breakthrough was reported on cycle 4 due to (1) a change in priority, (2) a shortage of funds, and (3) before sufficient information for design purposed could be examined.

Table 3 is a composite analyses of about 623 litres of barren effluent from the 150 ml-resin columns containing, in ppm, <0.10 CN_T, 5 to 40 NH_3, <0.03 Ni, <0.02 to 0.2 Cu and 0.01 to 0.4 Zn.

TABLE 3

Chemical Analysis of Alkaline-Cyanide Effluents from Ion-Exchange Treatment of Dome Cyanidation Wastes

Type of Analysis		Ion-Exchange Effluent
Total Cyanide (CN_T)	ppm	<0.10
CNS	"	4.3 - 70.0
Total S	"	120 - 150
Cu	"	0.02 - 0.2
Ni	"	<0.03
Zn	"	0.01 - 0.04
NH_3	"	5 - 40
Au	oz/T.	<0.003
pH		9.6 - 11.5

*See bottom of page 13.

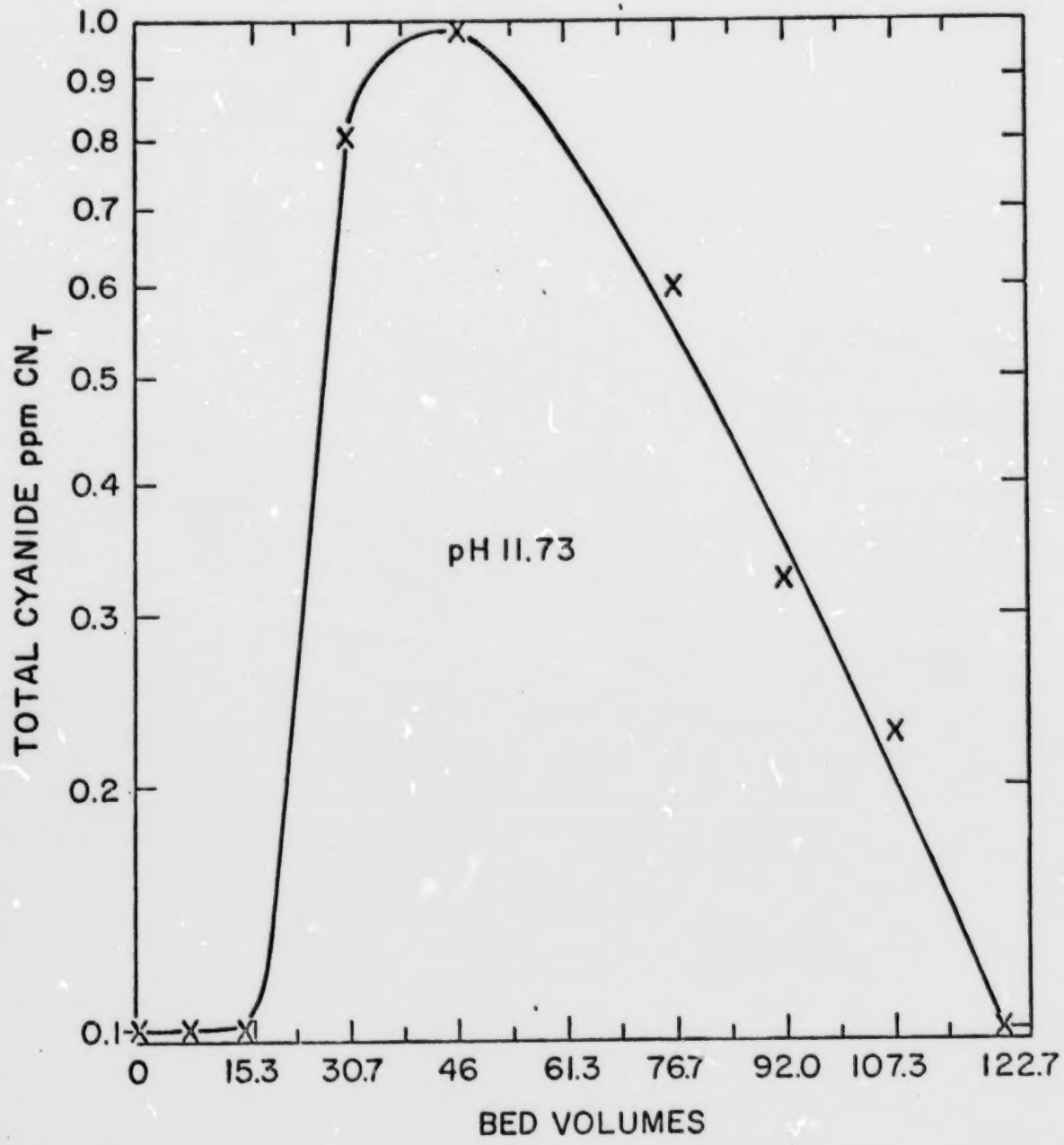

FIGURE 2

A "Royal Barren" Effluent Showing
Cyanide Concentration in the
Initial Stages of Cyclic Adsorption

*"Royal barren" is a volume of effluent, occurring during the early stage of adsorption, where influent anions flowing down the resin bed displace traces of residual cyanide anions remaining on the resin bed after previous desorption.

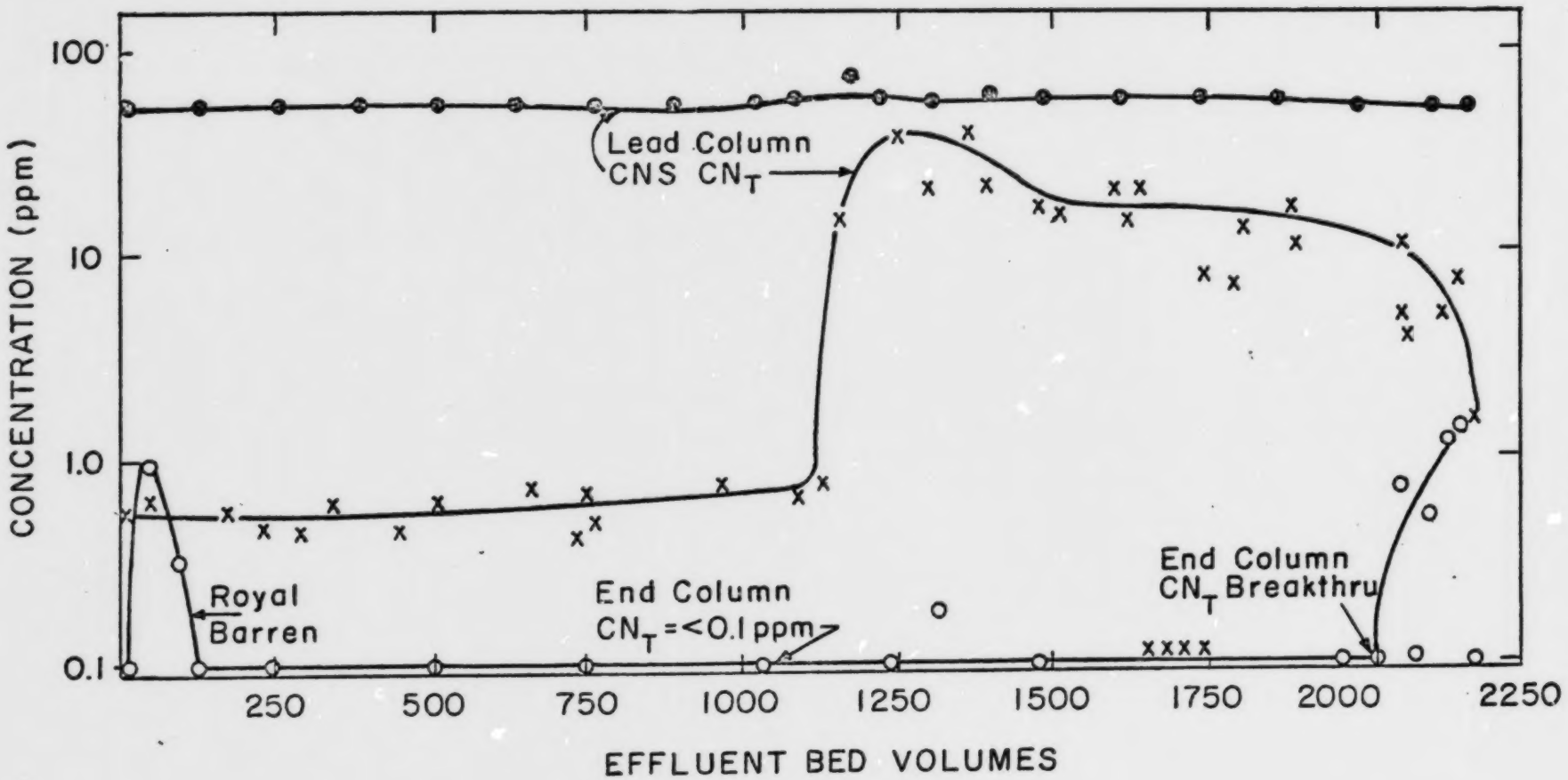

FIGURE 3

THE ADSORPTION OF DOME CYANIDE
ON RESIN COLUMNS D + A

Table 4 shows the source of influent to the adsorbing columns, and the disposal of the effluent during a proposed continuous series adsorption on two SO_4-form resin beds.

TABLE 4

A Typical Adsorption Loading
on Two SO_4-form Resin Columns

Influent Source	Effluent Bed Volumes	Disposal
Filter Press	≃ 15.3	To mill discharge or recycle.
	92	"Royal barren" recycled to cyanidation.
	170 to 2039	
Water	3.5	To mill discharge or recycle. pH 11.7 backwash containing ≃ 0.6 ppm CN_T to cyanidation.

(b) Desorption Phase

The results of the 1% H_2SO_4 desorption of cyanide are tabulated in Table 5. The first cycle desorption results showed that the fresh resin loading of 2.06 lb CN/cu ft was very similar to the 2 lb CN/cu ft obtained in the preliminary feasibility laboratory work[3]. The loading on fresh resin dropped to 0.51 lb CN/cu ft of resin in the second cycle. This decrease in loading was probably attributable to the lower volume throughput of feed waste during adsorption. The desorption plus water-wash periods, in the first two cycles, were of longer duration than the adsorption period.

The loading on fresh resin beds was 0.98 lb CN/cu ft for cycle 3. The flowrate of desorption and water-wash was increased slightly to close the time-lapse between the adsorption and desorption periods. Increasing the flow, however, did not reduce the water volume as the displacement of the bisulphate (HSO_4-) anion

TABLE 5

CYANIDE DESORPTION RESULTS

Cycle No.	Column	Retention Time (mins.) Nominal	Retention Time (mins.) Actual	Total Time Elution and Wash hrs.	Recycle Entering Volume Litre	Recycle Entering Volume Bed Vols.	Recycle Entering CN_T ppm	Recycle Entering CN_T gms	Hi-Grade CN_T ppm	Hi-Grade CN_T gms	Recycle Leaving Volume Litre	Recycle Leaving Volume Bed Vols.	Recycle Leaving CN_T ppm	Recycle Leaving CN_T gms	Caustic Trap gms CN	Resin Loading gms CN/ 150 ml.	Resin Loading lbs. CN/ cu ft	H_2SO_4 Make-up lbs. H_2SO_4/ lb. CN	Water Wash
1	A	8	8	29.13	7.15	47.7	-	-	660	4.73	5.96	39.7	34.7	0.207	0.0048	4.95	2.06	-	Wash=0.477g H_2SO_4/1. or 7.64 g H_2SO_4
				Wash 18	-	-	-	-	-	-	8.12	54.1	1.0	0.010	-	-	-	-	
2	B	8	7.8	28.47	7.15	47.6	-	-	166	1.18	5.96	39.7	2.6	0.15	0.0234	1.22	0.51	-	Wash=0.193 g/1 or Total=5.78g H_2SO_4
				Wash 33.3	-	-	-	-	-	-	15.0	100.0	<0.1	-	-	-	-	-	
3	C	6	6	22.07	9.40	62.7	5.4	0.052	315	2.27	6.06	40.4	20.7	1.125	0.0056	2.36	0.98	16.0	Wash=0.48 g/1 or Total=7.3g H_2SO_4
				Wash 12.5	-	-	-	-	-	-	15.0	100.0	0.49	0.015	-	-	-	-	
4	D	6	4.9	17.7	13.06	87.1	1.0	0.014	972	6.85	6.01	40.1	4.0	0.024	0.0155	7.14	2.98	15.26	Wash=0.44 g/1 or Total=4.88g H_2SO_4
				Wash 8.25	-	-	-	-	-	-	11.01	73.4	1.1	0.012	-	-	-	-	CN_T=1.10 ppm

from the resin is a time-consuming process. The concern here was to adequately wash the acidic anions from the resin to minimize the evolution of HCN gas on a subsequent cyanide adsorption. The effluent water-wash, containing low concentrations of acid and cyanide, presents a disposal problem, and so it is best regenerated with acid and recycled.

The highest fresh resin loading of 2.98 lb CN/cu ft on cycle 4 reflects the high-volume throughput of cyanidation waste on adsorption. The desorption flow was increased slightly from cycle 3. The upflow water-wash volume was reduced by washing to an effluent pH of about 4.0. This volume could be regenerated to 1% H_2SO_4 and recycled to a subsequent desorption. Any residual cyanide on the resin bed would be displaced on the subsequent adsorption as "royal barren" and recycled to cyanidation.

The gaseous HCN adsorbed in the caustic trap during adsorption over four cycles ranged from 0.09% to 1.9% of the cyanide loading, with a mean value of 0.22%. The acid consumption was 15.3 lb H_2SO_4/lb CN. In future studies, the acid consumption could possibly be reduced somewhat by attempting to decrease the volume of desorption effluent to alkali solution without loss of gaseous HCN to the working atmosphere. Alkali consumption would be included in cyanidation costs.

In Goldblatt's paper[2], he states, "the used acid tended to build-up" due to the variation in cyanide concentrations of the influent waste. A proposed desorption procedure is presented, in Table 6, as a guide for future investigations.

TABLE 6

A Proposed 1% H_2SO_4 Desorption and Wash of Cyanide-Loaded Anion Exchanger

Source	Bed Volumes		Disposal
	Influent	Effluent	
1% H_2SO_4 Recycle Tank	13.3		
Barren 1% H_2SO_4 Tank	73.3	73.3	Cyanide adsorbed in alkaline media and recycled to cyanidation.
		13.3	Recycle tank as 1% H_2SO_4 for next desorption.
Water Tank Wash to ≈pH 4.0	73.3		
		73.3	Barren tank-regenerated to 1% H_2SO_4 for next desorption.
Total	159.9	159.9	

The recycling of regenerated wash solutions would avoid a build-up of acid solution and eliminate a disposal problem. Any residual cyanide on the resin bed after water-wash of ≈ 73 bed volumes would be displaced in the early stages of the next adsorption on that resin bed as the "royal barren", and recycled to cyanidation.

THE RECOVERY OF THE METAL CATIONS

The Dome heavy metals were desorbed from the cation exchanger with a 1.7N NaCl desorbent acidified to pH 2.0 with H_2SO_4. Ten bed volumes were required, at a flow rate of 0.05 bed volumes/min. The metal (M) loadings of the IR 120 columns were the equivalent of 0.675, 0.157, 0.26 and 1.12 lb M/cu ft resin respectively for cycles 1 to 4 where M = total of Cu, Zn and Ni. These loadings reflect the volume of cyanidation waste fed through the anion exchanger adsorption columns. However, the loadings are low. These cation columns could probably be desorbed after every second or third adsorption as they are capable of loadings of ≈2 lb M/cu ft. Higher loadings would make more efficient use of desorption reagents. The average metal loading was 0.32 lb M/lb CN over the four adsorption cycles.

The first three desorption bed volumes of cycles 1 and 3 were composited and neutralized to pH 8.0 with Na_2CO_3 to produce a bulk product of the metals. The product after washing, drying and calcining at 500°C. was, in percent, 5.4 Cu, 19.58 Ni and 49.33 Zn, or the equivalent of 93.08% CuO + NiO + ZnO. The metals in the strong fraction of cycle 2 were not precipitated as the metal content was very low and non-representative due to the low adsorption throughput volume of cyanidation waste.

The IR 120 column of cycle 4 was eluted with 1.7N NaCl, unacidified, to reduce the Na_2CO_3 consumption. Neutralization of the first three bed volumes with Na_2CO_3, as above, followed by filtration, washing, drying and calcining gave a bulk product, in percentage, of 18.0 Cu, 43.21 Ni and 13.84 Zn. The oxide equivalent was 94.75% CuO + NiO + ZnO.

Desorption reagent consumptions were 0.56 lb NaCl/lb CN and 3.29 lb Na_2CO_3/lb CN.

DISCUSSION

This investigation has shown the capability of ion-exchange technology to decrease the cyanide concentration of gold wastes to <0.1 ppm CN_T at high adsorption flowrates of 6.54 litres/hr or the equivalent of 4.53 gals/min/cu ft through 150 ml beds of SO_4- form resin. The 150-ml exchanger bed, in the end and the lead column positions, adsorbed essentially all cyanide (CN_T) from almost 3000 bed volumes of the Dome waste.

This is the initial attempt, that this writer is aware of, to use SO_4- form strong-base resins for the removal of free cyanide and metal-cyanide complexes from a complex cyanidation waste in order to meet an environmental standard of <0.1 ppm CN_T. The advantage of using SO_4- columns is that sulphuric acid and water, two of the least expensive desorption reagents, are readily available to most northern gold operations in Canada. In Ontario, the acid is anticipated to be available from the Texas Gulf operation in the Timmins area. The easy availability of the acid to the gold operation reduces transportation cost of the reagent for cyanide removal.

E. Goldblatt wrote[8] in 1956, "with the large number of simple and complex anions present, considerable physico-chemical study is required to elucidate more clearly the equilibria that exist between the anions and the resin bed". Twenty years later that clarification is still required. There is ample competition for resin sites in complex systems such as exist in cyanidation wastes with free cyanide, thiosulphate, sulphate and six or more metal-cyanide complex anions. This competition affects the exchange rates and the estimation of suitable flowrates. The concentration of each of the complex anions of interest, plus the competition from the extraneous anions (e.g. thio-compounds and sulphates), has to be considered for each waste solution. The multiplicity of anions and their concentrations can very considerably in a variety of waste solution. The multiplicity of anions and their concentrations can vary considerably in a variety of waste solutions from different operations. The results and conclusions here relate only to the Dome waste and should not be interpreted as indicative of the behavior of all cyanidation wastes.

A. Himsley and E.J. Farkas[9] have written that there is "no known method of calculating the precise behavior of an ion-exchange resin under complex conditions". Design data, such as operating resin capacity, optimum contact time, reagent consumption, and resin poisoning can only be determined satisfactorily by approximately 25 adsorptions and desorptions per column[10].

Caustic (NaOH) was used as the HCN-absorbent in this work, as the scaling-down to laboratory scale of a lime absorption process for gaseous hydrocyanic acid (HCN) is reported to present problems. Lime (CaO) is commonly used in gold cyanidation, due to its low cost, to maintain a high alkalinity, "but its use[11] necessitates the installation and maintenance of a proper slaking operation, which is an economic disadvantage for small operations. Sludge and scaling problems must be considered when using lime" to treat solutions containing sulphates, etc.

In practise, the cyanide would be recovered as $Ca(CN)_2$ by feeding the desorption effluent, containing about 5 g. CN/litre in dilute H_2SO_4, from the column to a lime neutralizer. The clear $Ca(CN)_2$ supernatant would be recycled to the cyanidation circuit after the suspended solids of gypsum and excess lime have settled. The slow settling of gypsum and free lime solids would interfere with solution sampling during the laboratory investigation. Normally, the addition of acid to cyanide solutions is not recommended as toxic hydrocyanic acid gas (HCN) is evolved. If the neutralizer can be maintained at a high alkalinity of about pH 12, the gas evolution is minimal. Lime is "easier to handle on a mill scale than on a laboratory scale" due, (1) to its

"time-lag" conversion from low soluble lime to gypsum, (2) to the relatively large volumes of water required to transport $Ca(OH)_2$ (solubility 0.18%), excess CaO (solubility 0.13 to 0.15%), and the gypsum product. However, the more reactive caustic adsorbs the HCN gas easily and safely up to a concentration of about 5 g CN/litre and at a pH of ≈14. This reagent minimizes losses of toxic cyanide gas to the working atmosphere.

V.M. Brown[12], in a discussion on analytical aspects of toxicity of substances to fish, writes that "no matter how skilled or industrious the chemist, he can never analyze continuously for only those substances present at individually potentially harmful concentrations". M. Hofton[13] follows up with "the highly toxic cyanide ion is one of the most difficult species to determine in complex liquors, particularly at low levels". The specific-ion electrodes presently available for cyanide determination are handicapped by membrane erosion and ion interference. Hofton describes a 2-week application of an Ag-ion selective-monitor for the continuous determination of free cyanide in steel-mill effluents, down to a concentration of 0.095 ppm CN. A $CaCO_3$ coating formed in the cell and the tubing, but no abrasion of the electrode crystal was observed. The application of this Ag-ion selective-electrode may prove beneficial to future investigations on cyanidation wastes by monitoring the low-level cyanide concentration of ion-exchange effluents to breakthrough. This application would reduce the analytical load of samples to the analysts and result in efficient process control.

A comparison should be made of the $AgNO_3$-titrimetric method[6] versus the picric acid[4] method as used for the analyses of high concentration of cyanide up to 4 to 5 g CN/litre. The picric acid method is, basically, a low CN-concentration method at alkalinities equivalent to 0.025 M $Na_2 CO_3$. "A slight decrease in colour intensity"[4] may be developed in the picric acid colorimetric method due to the strong alkalinity of 0.7 to 1.4 N NaOH in desorption samples.

Information gathered from the following suggested studies would be valuable to processors, laboratory investigators, and analysts alike. Some of these techniques are discussed verbally and practised in cyanide milling operations but the technology does not seem to have been transferred in any detail:

1. the solubility of cyanide in various concentrations of H_2SO_4, eg. 1% H_2SO_4;

2. the solubility of (a) HCN gas and (b) the HCN + 1% H_2SO_4 mixture in lime slurries;

3. an investigation of the factors involved in the stability of cyanide in some cyanidation wastes, with some means of controlling the latter during an investigation;

4. the effect of very low and very high concentrations of the ferro- and ferri- cyanide complexes, (ie. $[Fe(CN)_6^{3-}]$ and $[Fe(CN)_6^{4-}]$ respectively on the adsorption efficiency of the anion exchanger for other metal-cyanide complexes and free cyanide. A parallel study of the effect of these ferro- and ferri-cyanide complexes on the various analytical cyanide procedures would be elucidating.

ECONOMIC EVALUATION

The Dome filter press effluent, containing 14.4 to 67.0 ppm total cyanide (CN_T), discharges to the environment at ≈125 Igpm. The amount of cyanide discharged annually, as free cyanide and metal-complexed cyanide, is almost 27,000 lb CN_T or the equivalent of 50,000 lb NaCN/year. This constitutes, at $0.34/lb NaCN, an annual loss of ≈$17,000.

An estimated capital cost of $188,000 is required to remove an average concentration of 40.7 ppm CN_T and 10 to 29 ppm of heavy metals Cu, Ni and Zn from the Dome alkaline cyanide waste by ion-exchange. This estimate is based on a pilot-plant study of limited duration using 150-ml columns and includes the installation of anion and cation exchange columns with resin, tanks, filter, pumps, piping, instrumentation, engineering and contingences.

Operating costs are shown in Table 7 with capital costs depreciated over 10 years.

TABLE 7

An Estimate of Costs for the Ion-Exchange Removal of Cyanide and Heavy Metals from a Dome Filter Press Effluent

Capital Cost*	$0.37/lb. NaCN
Operating Costs	
Resin Loss**	$0.04/lb. NaCN
Labour***	0.48 "
Reagents****	
H_2SO_4, NaCl & Na_2CO_3	0.45 "
Total Operating	$0.97 "
Total Operating & Capital Cost	$1.34/lb. NaCN
Estimated annual cost of operation	$68,000.
Reuse of NaCN @ $0.34/lb	17,000.
Estimated net cost annually ie. $1.88/lb CN_T or $0.77/1000 gal	$50,900.

*Includes 4 anion exchange columns with 50 cu ft column @ $90/cu ft resin + 2 cation exchange columns with 36 cu ft resin/column @ $43/cu ft resin.

**Loss estimated @ 10%/year for anion and 3%/year for cation exchangers.

***Includes 2 operators, 1 skilled @ $5.78/hr and 1 unskilled @ $4.78/hr on an afternoon or morning shift and alternate weekends.

****Reagents costs: H_2SO_4 @ 2¢/lb.
NaCl @ 2¢/lb.
and Na_2CO_3 @ 2.8¢/lb.

The recycled cyanide has a monetary value. The annual disposal of 6.4 tons of heavy metals, also having an estimated value of ≈$10,000. will have to be considered and negotiated.

CONCLUSIONS

The study has demonstrated the chemical feasibility of adsorbing free cyanide and heavy-metal cyanide complexes on

SO_4- form anion exchanger in fixed beds,

1) almost 3000 bed volumes of the cyanidation waste were put through 150 ml resin beds of Amberlite IRA-400 before CN_T-breakthrough at 0.1 ppm CN_T.

2) cyanide loadings of up to almost 3 lb CN/cu ft resin were obtained.

3) flowrates of up to 6.54 litres/hr or the equivalent of 4.53 gals/min/cu ft through the 150 ml-columns were achieved, to produce an effluent of <0.1 ppm CN_T.

4) the investigation was terminated due to financial and time limitations.

5) capital and operating costs, based on the limited amount of work accomplished, were estimated at $1.34/lb NaCN recovered.

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ACKNOWLEDGEMENTS

Grateful acknowledgement is extended to the following personnel for their assistance in this work:

1. to Mr. J.L. Fleury, who arranged the equipment, performed the sampling and laboratory duties, offered constructive suggestions, and co-operated fully during the course of this investigation;
2. to the analysts in the control laboratory, under Mr. R.J. Guest and Mr. D. Barkley, who supplied the analytical data.